

The Electronic and Thermoelectric Properties of $\text{Si}_{1-x}\text{V}_x$ Alloys from First Principles

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The effect of temperature and vanadium metal concentration on the electronic and thermoelectric properties of Si in the diamond cubic structure has been investigated using a combination of density functional theory simulations and the semi classical Boltzmann's theory. The BotzTrap code within the constant relaxation time approximation has been used to obtain the Seebeck coefficient and other transport properties of interest for alloys of the structure $\text{Si}_{1-x}\text{V}_x$, where x is 0, 0.125, 0.25, 0.375, and 0.5. The thermoelectric properties have been extracted for a temperature range of 300 K to 1,000 K. The general trend with V atom substitution for Si causes the Seebeck coefficient to increase and the thermal conductivity to decrease for the various alloys. The optimum values are for Si_5V_3 and Si_4V_4 alloys for charge carrier concentrations of 10^{21} cm^{-3} in the mid temperature range of 500~800 K. This is a very desirable effect for a promising thermoelectric and the figure of merit ZT approaches 0.2 at 600 K for the p-type Si_5V_3 alloy.

Key Words: Thermopower, Si, Thermal conductivity, Vanadium, Local density approximation

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INTRODUCTION

The last decade has seen a renewed interest in thermoelectric (TE) materials. The stimulus to the interest in this class of materials is the recent progress in improving the efficiency of energy conversion by a variety of techniques. The direct conversion of heat energy to electricity using TE is a very appealing option, especially as currently there is a lot of heat energy wasted during the consumption of energy resources (Bell, 2008; Zhang & Zhao, 2015). Although, TEs offer many advantages like lack of dependence on heat source, lack of maintenance, etc. the major drawback of the low efficiency for energy conversion has kept this technology on hold.

A quantity ZT called figure of merit, measures the efficiency of conversion for TE materials and is given by the equation

$$ZT = S^2 \sigma T / \kappa. \quad (1)$$

Where S is the Seebeck coefficient, σ is the electrical

conductivity, T is the temperature in Kelvin and κ is the total thermal conductivity consisting of the electronic part κ_e and the lattice part κ_l . In order to improve the performance of TE materials, the power factor $S^2 \sigma$ and κ need to be optimized to the maximum and minimum values respectively. This is easier said than done as the Wiedemann-Franz law requires the electronic part of thermal conductivity (κ_e) to be proportional to electrical conductivity (σ),

$$\kappa_e = L \sigma T. \quad (2)$$

L is the Lorenz number. Also, there are limits to increasing S and σ simultaneously. Several different strategies have been adopted to enhance ZT to values greater than 1, namely, size effect (Heremans et al., 2013; Hicks & Dresselhaus, 1993), doping and carrier concentrations (Jaiyaraman et al., 2016; Pei et al., 2011; Yuli et al., 2016), Nano-structuring (Biswas et al., 2012; Hsu et al., 2004) etc.

Silicides of transition metals have been investigated as high

potential TEs (Arita et al., 2001; Gu et al., 2002; Ivanenko et al., 2003) especially for the mid-temperature range of 300 K to 700 K. The ZT values attained for Rh-doped Ru_2Si_3 (Arita et al., 2001) is larger than the optimized n-type SiGe by 50%. This encourages us to investigate compounds of Si with the transition metal vanadium. Vanadium is as common as Cu and Zn and is the 22nd most abundant metal in the earth's crust. The present study is an investigation of the TE properties of $\text{Si}_{1-x}\text{V}_x$ alloys formed by substitution of V atoms for Si in the conventional unit cell of Si in the diamond cubic structure of 8 atoms. The Si:V stoichiometric ratios in the alloys are 1:0, 7:1, 3:1, 5:3, and 1:1 with $x=0, 0.125, 0.25, 0.375$, and 0.5 respectively.

MATERIALS AND METHODS

The electronic properties of $\text{Si}_{1-x}\text{V}_x$ alloys in the diamond cubic structure is calculated with the ABINIT software package (Gonze et al., 2005) using density functional theory (DFT) under the local density approximation (LDA). The Troullier-Martins pseudopotential with core corrections (Perdew & Wang, 1992) is used for Si and for V we have used the HGH pseudopotentials (Hartwigsen et al., 1998). As in our previous works (Ramanathan, 2013; Ramanathan & Khalifeh, 2017) a convergence criteria of less than 1×10^{-6} Ha for total energy differences in the self-consistent field is used for the optimization of cutoff energy, kpoint grid, lattice parameter and all structural calculations. The optimized Si lattice constant obtained for the structure is 10.18 Bohr which is close to experimental value of 10.23 Bohr and is used for the supercell to better compare with available experimental TE properties of pure Si as a test of the accuracy of our method. A sufficiently dense k-point grid of $21 \times 21 \times 11$ with a cutoff energy of 14 Ha and 100 bands is used with the BoltzTraP code (Madsen & Singh, 2006) to extract the TE properties using a 1×1 supercell. The code solves the

Boltzmann transport equation under the constant relaxation time (τ) approximation (RTA). Under this approximation the electrical/thermal conductivity distribution is given by the equations below, where, f is the electronic distribution at equilibrium, μ is the chemical potential, e is the charge of electron, T is the temperature, ϵ the electron energy and Ω is the unit cell volume of the crystal.

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \int_{-\infty}^{+\infty} \sigma_{\alpha\beta}(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon \quad (3)$$

$$\kappa_{\alpha\beta}^e = \frac{1}{e^2 T \Omega} \int_{-\infty}^{+\infty} \sigma_{\alpha\beta}(\epsilon) (\epsilon - \mu)^2 \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon \quad (4)$$

Taking into account the symmetry of the system BoltzTrap performs Fourier expansion of the band energies to obtain the transport coefficients. Under the constant RTA S and ZT are independent of τ and can be obtained as a function of the chemical potential or temperature. The electrical/thermal conductivities and also the power factor are dependent on τ

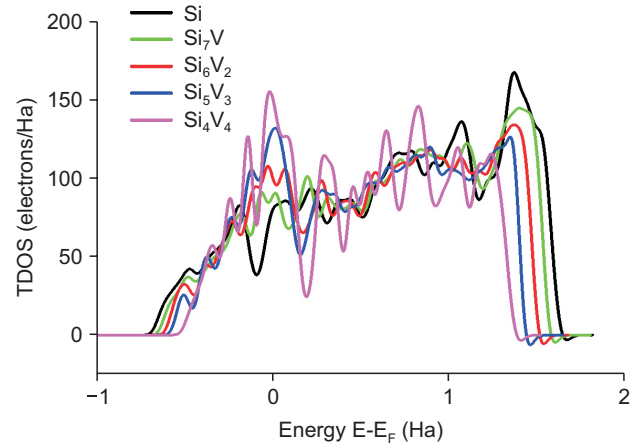


Fig. 1. The total density of states (TDOS) for the different alloys.

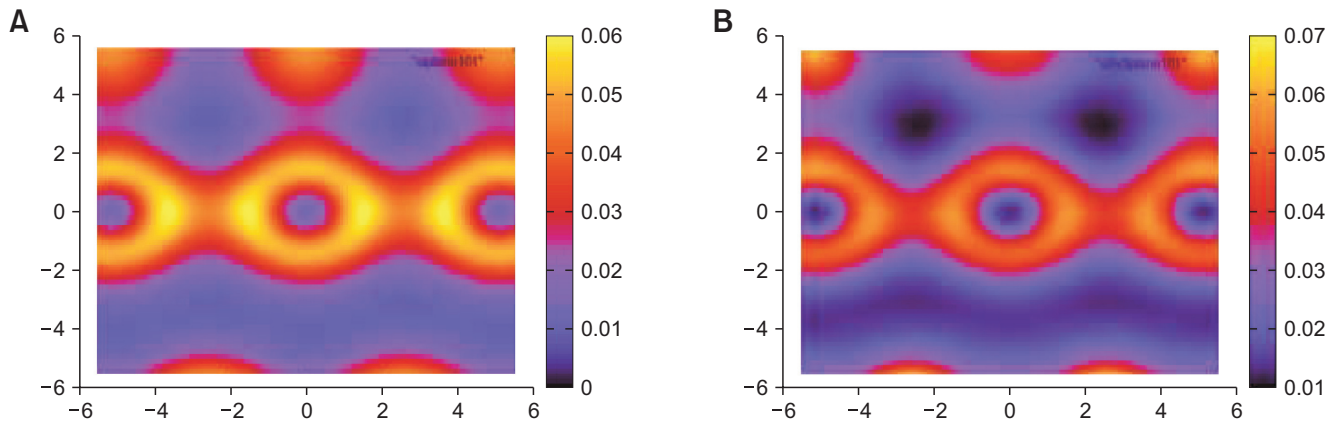


Fig. 2. Two dimensional charge density plot along the 101 plane of the Unit cell for (A) Si and (B) Si_5V_3 alloy.

and can be obtained only in terms of τ . So in order to obtain their actual values one has to depend on the experimental values of τ for the same or similar system. All the results except the Seebeck and ZT have been given in terms of τ , since no experimental values are available for the silicon-vanadium alloys under consideration.

RESULTS AND DISCUSSION

DFT calculations followed by BoltzTrap as implemented in the Abinit code is performed for the supercell of varying V atom concentrations in the diamond cubic conventional unit cell. The V atom size is comparable to that of Si and this permits the formation of substitution alloy. The V atoms in the alloys occupy inner positions on the body diagonals of the unit cell. The number of electrons at the Fermi level and the Fermi energy increases with each substitution of a Si atom with a V atom in the Si-V alloys. This is clearly seen in the total density of states (TDOS) plot, namely Fig. 1. The peak at the Fermi energy is maximum for Si_4V_4 and minimum for Si. The charge density color plot along the 101 plane is shown for the pure Si and the alloy Si_5V_3 in Fig. 2. The central point of the plane is 0 0 0 and the right hand scale shows the colors related to the regions of maximum and minimum charge density. The subsequent change in the charge density and the total DOS with each replacement of a Si with a V atom alters the transport properties and gives a more desirable trend for TE applications.

The two-dimensional total charge density plot along the 101 plane for (A) Si and (B) Si_5V_3 of the Si-V alloys is shown in Fig. 2.

The TE properties extracted using the BoltzTrap code for a charge carrier concentration of 10^{21} cm^{-3} is displayed in the subsequent graphs. The Seebeck characteristics at a

temperature of 300 K for the different alloys as a function of the chemical potential are displayed in Fig. 3. We see that the maximum values are for Si_5V_3 in blue color. The bulk Si Seebeck coefficient obtained is 392 $\mu\text{V/K}$ which compares well with the experimental value of 435 $\mu\text{V/K}$ (Lasance, 2006). The effect of temperature on the Seebeck coefficient and the thermal conductivities for the different alloys is shown in Fig. 4A and B respectively. The optimum values of the transport properties at each temperature is extracted and displayed as a function of temperature. The thermal conductivities are given in terms of τ . In Fig. 4A the modulus of the Seebeck coefficient is plotted since we have both positive and negative values for the different alloys. We see an increase with temperature of the Seebeck coefficient for all the alloys. The maximum values are for Si_5V_3 followed by Si_4V_4 with appealing TE properties in the mid temperature range. This is very encouraging as the mid temperature is where most of the industrial processes

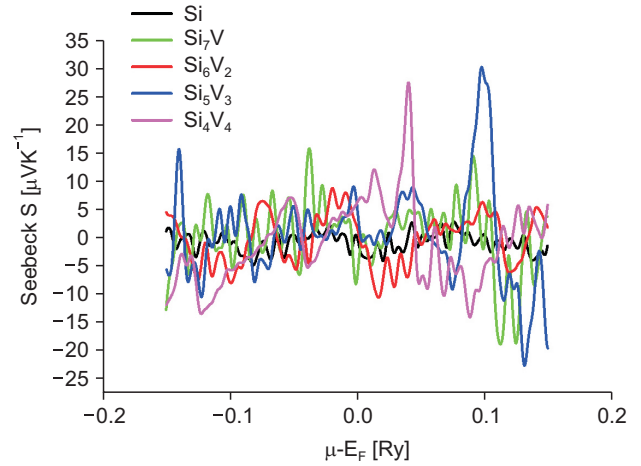


Fig. 3. The Seebeck coefficient as a function of the chemical potential.

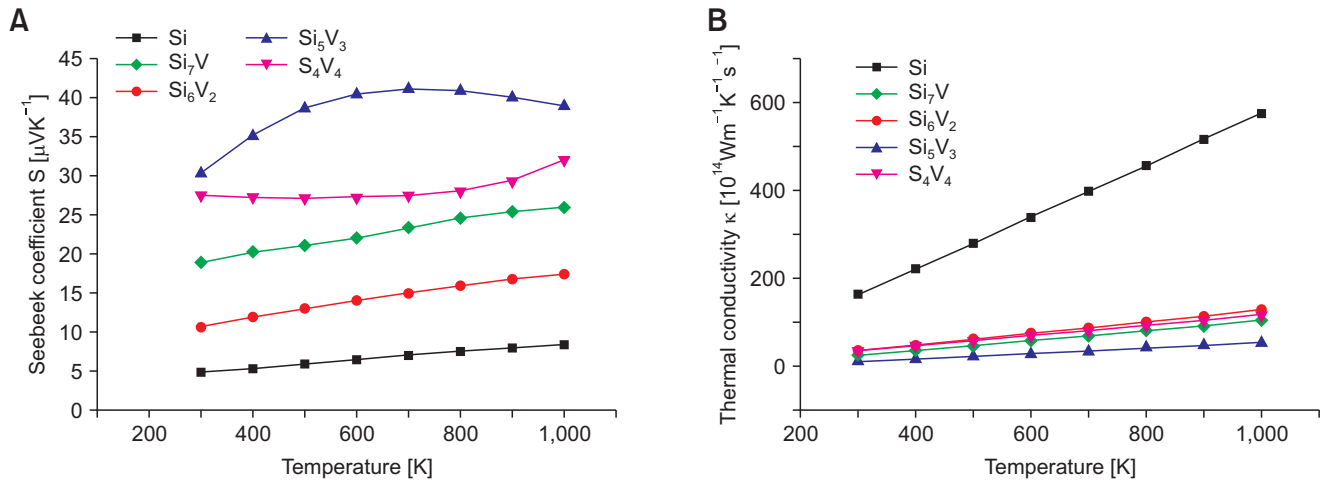


Fig. 4. Seebeck S (A) and thermal conductivity κ (B) as a function of temperature.

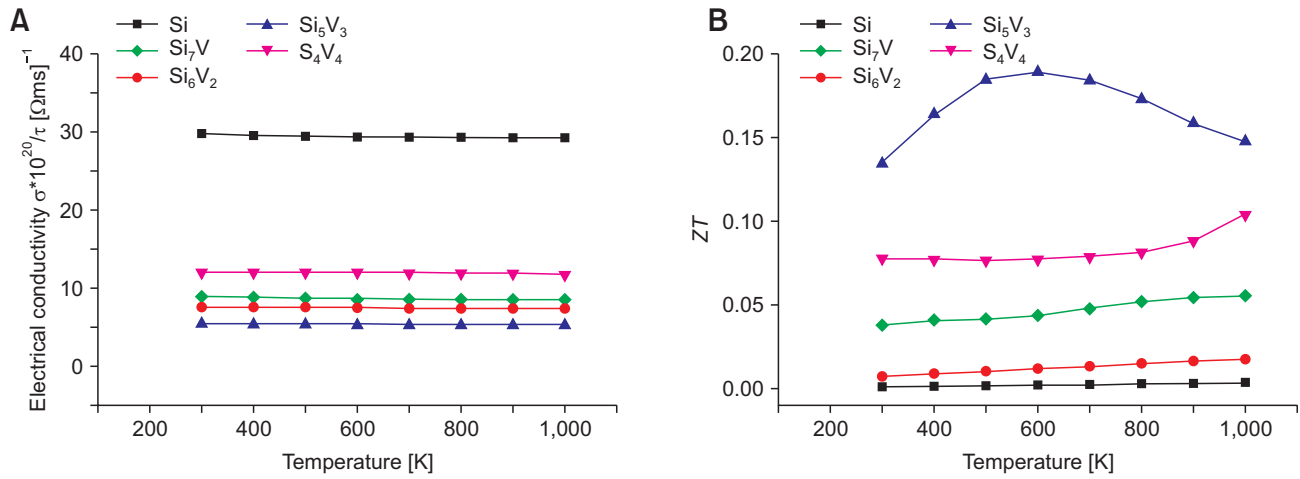


Fig. 5. Electrical conductivity (A) and figure of merit ZT (B) as a function of temperature.

operate. The size and sign of the of the Seebeck coefficient are related to the electron distribution asymmetry around the Fermi level. The sign of S determines if the material is n-type or p-type TE at a given temperature and whether the charge carriers are electrons or electron holes. Our results show that negative Seebeck coefficient predominates for Si, Si₇V and Si₆V₂ whereas Si₅V₃ has positive values throughout the temperature range. On the other hand Si₄V₄ has positive and negative values, and for temperatures greater than 800 K negative S predominates. The thermal conductivity is considerably lowered by alloying with V and we find that the lowest value is for Si₅V₃ as shown in Fig. 2B. Si₄V₄, Si₆V₂ and Si₇V show slightly higher values of the thermal conductivities but, pure Si on the other hand, has a very sharp increase and the maximum values is for Si. The calculated value of thermal conductivity for pure Si alloy is 164 W/mK at 300 K using a typical relaxation time τ of 10^{-14} s and this compares well with the available technical data (<http://periodictable.com/Elements/014/data.html>) of 150 W/mK. With low thermal conductivities and high Seebeck coefficients for Si₅V₃ and Si₄V₄ the recipe for optimizing the figure of merit ZT will be complete provided the electrical conductivities for these two alloys are also comparatively high.

The electrical conductivities σ in terms of τ and the figure of merit ZT are plotted as a function of temperature for the different alloys in Fig. 5A and B respectively. From the Figure it is clear that the electrical conductivities are not affected by the temperature and are almost constant. The maximum values are for Si followed by Si₇V. Although, Si₅V₃ and Si₄V₄ have lower values of σ the best combination of S , σ and κ are for Si₅V₃ and Si₄V₄. The highest value of ZT is for Si₅V₃ followed by Si₄V₄. This is due to the combination of high Seebeck and low thermal conductivity for these alloys. This is seen in Fig. 5B with the optimum values in the mid

temperature range reaching 0.2 for Si₅V₃ and around 0.1 for Si₄V₄. The figure of merit is almost constant with temperature for pure Si, Si₇V and Si₆V₂ and is comparatively lower than the other alloys.

CONCLUSIONS

The TE properties of the Si_{1-x}V_x alloys in the diamond cubic structure have been investigated using DFT-LDA pseudopotentials and the BoltzTrap code. The study has provided useful insight regards the best stoichiometric ratio of Si:V that enhances the TE performance of these alloys. We find very promising TE properties for Si₅V₃ and Si₄V₄ which show appreciable ZT values. This leads to the conclusion that a 37.5% vanadium Si₅V₃ alloy is the best choice for p-type TE operating in the mid temperature range 500 K~800 K. As a first study, the findings will help establish a data base for future investigations and proof of possibility of high TE efficiency with this class of materials. Further experimental and theoretical investigations to verify the result and establish the best Si:V ratio lying between Si₅V₃ and Si₄V₄ are required.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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REFERENCES

- Arita Y, Mitsuda S, Nishi Y, Matsui T, and Nagasaki T (2001) Thermoelectric properties of Rh-doped Ru_2Si_3 prepared by floating zone melting method. *J. Nucl. Mater.* **294**, 202.
- Bell L E (2008) Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. *Science* **321**, 1457-1461.
- Biswas K, He J, Blum I D, Wu C I, Hogan T P, Seidman D N, Dravid V P, and Kanatzidis M G (2012) High performance bulk thermoelectrics with all-scale hierarchical architectures. *Nature* **489**, 414-418.
- Gonze X, Rignanese G-M, Verstraete M, Beuken J-M, Pouillon Y, Caracas R, Jollet F, Torrent M, Zerah G, Mikami M, Ghosez P, Veithen M, Raty J-Y, Olevano V, Bruneval F, Reining L, Godby R, Onida G, Hamann D R, Douglas C, and Allan D C (2005) A brief introduction to the ABINIT software package. *Kristallogr* **220**, 558-562.
- Gu J-J, Kuwabara K, Tanaka K, Inui H, Yamaguchi M, Yamamoto A, Ohta T, and Obara H (2002) Crystal structure and thermoelectric properties of $\text{ReSi}_{1.75}$ silicide. *MRS Proc.* **753**, 501.
- Hartwigsen C, Goedecker S, and Hutter J (1998) Relativistic separable dual-space Gaussian pseudopotentials from H to Rn. *Phys. Rev. B* **58**, 3641.
- Heremans J P, Dresselhaus M S, Bell L, and Morelli D T (2013) When thermoelectrics reached the nanoscale. *Nat. Nanotechnol.* **8**, 471-473.
- Hicks L D and Dresselhaus M S (1993) Thermoelectric figure of merit of a one-dimensional conductor. *Phys. Rev. B* **47**, 16631-16634.
- Hsu K F, Loo S, Guo F, Chen W, Dyck J S, Uher C, Hogan T, Polychroniadis E K, and Kanatzidis M G (2004) Cubic AgPbmSbTe_{2+m} : bulk thermoelectric materials with high figure of merit. *Science* **303**, 818-821.
- Ivanenko L, Filonov A, Shaposhnikov V, Krivosheev A, Behr G, and Souptel D (2003) Thermoelectric properties of Mn-doped Ru_2Si_3 . In: *Proc. 22nd Int. Conf. Thermoelectrics*, pp. 157-160 (IEEE).
- Jaiyaraman A, Kademane A B, and Molli M (2016) DFT study on the carrier concentration and temperature-dependent thermoelectric properties of antimony selenide. *Indian Journal of Material Science* Article ID 7296847, 7 pages.
- Lasance C J M (2006) Design, Number 4, Technical Data, Test & Measurement, Volume 12 [internet]. Available from: <https://www.electronics-cooling.com/2006/11/the-seebeck-coefficient/>.
- Madsen G K H and Singh D J (2006) A code for calculating band structure dependent quantities. *Comput. Phys. Commun.* **175**, 67-71.
- Pei Y Z, Shi X, LaLonde A, Wang H, Chen L, and Snyder G J (2011) Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* **473**, 66-69.
- Perdew J P and Wang Y (1992) Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **45**, 13244.
- Ramanathan A A (2013) A DFT calculation of Nb and Ta (001) Surface Properties. *JMP* **4**, 432-437.
- Ramanathan A A and Khalifeh J M (2017) Substrate matters: magnetic tuning of the Fe monolayer. *JMMM* **426**, 450-453.
- Yuli Y, Zhang G, Wang C, Peng C, Zhang P, Wang Y, and Ren W (2016) Optimizing the Dopant and Carrier Concentration of $\text{Ca}_5\text{Al}_2\text{Sb}_6$ for High Thermoelectric Efficiency. *Scientific Reports* **6**, 29550.
- Zhang X and Zhao L-D (2015) Thermoelectric materials: energy conversion between heat and electricity. *Journal of Materiomics* **1**, 92-105.